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#4

CLAIM OF PRIORITY

Sir:

Applicants in the above-identified application hereby claim the right of priority in connection with Title 35 U.S.C. § 119 and in support thereof, herewith submit a certified copy of Finnish Patent Application No. 20002865, filed December 28, 2000.

Respectfully submitted

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PRIORITY DOCUMENT

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Hakija
Applicant

Xyrofin Oy
Kotka

Patenttihakemus nro
Patent application no

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Kansainvälinen luokka
International class

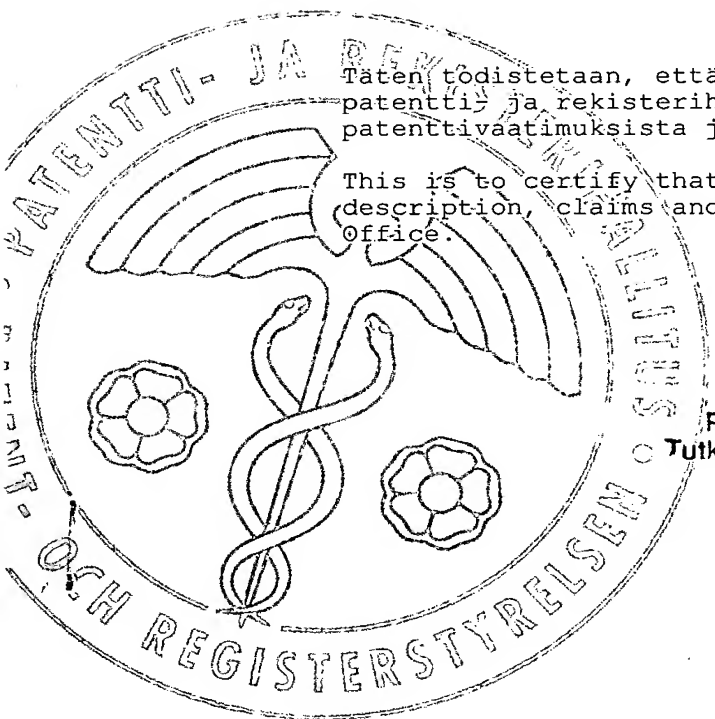
C13K

Keksinnön nimitys
Title of invention

"Separation Process"
(Erotusmenetelmä)

Täten todistetaan, että oheiset asiakirjat ovat tarkkoja jäljennöksiä patentti- ja rekisterihallitukselle alkuaan annetuista selityksestä, patenttivaatimuksista ja tiivistelmästä.

This is to certify that the annexed documents are true copies of the description, claims and abstract originally filed with the Finnish Patent Office.



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Specification

Title of the Invention

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Separation Process

Background of the Invention

The invention relates to a novel process of separating chemical compounds having a small molar mass from compounds having only a slightly larger molar mass. Especially, the invention relates to a novel process for recovering xylose from biomass hydrolysates, such as a spent liquor obtained from a pulping process, typically from a sulphite pulping process.

Xylose is a valuable raw material in the sweets, aroma and flavoring industries and particularly as a starting material in the production of xylitol. Xylose is formed in the hydrolysis of xylan-containing hemicellulose, for example in the direct acid hydrolysis of biomass, in enzymatic or acid hydrolysis of a prehydrolysate obtained from biomass by prehydrolysis (with steam or acetic acid, for instance), and in sulphite pulping processes. Vegetable material rich in xylan include the wood material from various wood species, particularly hardwood, such as birch, aspen and beech, various parts of grain (such as straw and husks, particularly corn and barley husks and corn cobs and corn fibers), bagasse, cocoanut shells, cottonseed skins etc.

Xylose can be recovered by crystallization e.g. from xylose-containing solutions of various origin and purity. In addition to xylose, the spent sulphite pulping liquors contain, as typical components, lignosulphonates, sulphite cooking chemicals, xylonic acid, oligomeric sugars, dimeric sugars and monosacharides (other than the desired xylose), and carboxylic acids, such as acetic acid, and uronic acids.

Before crystallization, it is as a rule necessary to purify the xylose-containing solution obtained as a result of the hydrolysis of cellulosic material to a required degree of purity by various methods, such as filtration to remove mechanical impurities, ultrafiltration, ion-exchange, decolouring, ion exclusion or chromatography or combinations thereof.

Xylose is produced in large amounts in pulp industry, for example in the sulphite cooking of hardwood raw material. Separation of xylose from such cooking liquors is described, for example, in U.S. Patent 4,631,129 (Suomen

Sokeri Oy). In this process, sulphite spent liquor is subjected to two-step chromatographic separation to form substantially purified fractions of sugars (e.g. xylose) and lignosulphonates. The first chromatographic fractionation is carried out using a resin in a divalent metal salt form, typically in a calcium salt form, and the second chromatographic fractionation is carried out using a resin in a monovalent salt form, such as a sodium salt form.

U.S. Patent 5,637,225 (Xyrofin Oy) discloses a method for the fractionation of sulphite cooking liquor by a sequential chromatographic simulated moving bed system comprising at least two chromatographic sectional packing material beds, where at least one fraction enriched with monosaccharides and one fraction enriched with lignosulphonates is obtained. The material in the sectional packing material beds is typically a strongly acidic cation exchange resin in Ca^{2+} form.

U.S. Patent 5,730,877 (Xyrofin Oy) discloses a method for fractionating a solution, such as a sulphite cooking liquor, by a chromatographic separation method using a system comprising at least two chromatographic sectional packing beds in different ionic forms. The material of the sectional packing bed of the first loop of the process is essentially in a divalent cation form, such as in Ca^{2+} form, and in the last loop essentially in a monovalent cation form, such as in Na^+ form.

WO 96/27028 (Xyrofin Oy) discloses a method for the recovery of xylose by crystallization and/or precipitation from solutions having a comparatively low xylose purity, typically 30 to 60 % by weight of xylose on dissolved dry solids. The xylose solution to be treated may be, for example, a concentrate chromatographically obtained from a sulphite pulping liquor.

It is also known to use membrane techniques, such as ultrafiltration to purify spent sulphite pulping liquors (e.g. Papermaking Science and Technology, Book 3: Forest Products Chemistry, p. 86, ed. Johan Gullichsen, Hannu Paulapuro and Per Stenius, Helsinki University of Technology, published in cooperation with the Finnish Paper Engineer's Association and TAPPI, Gummerus, Jyväskylä, Finland, 2000). High-molar-mass lignosulphonates can thus be separated by ultrafiltration from the low-molar-mass components, such as xylose.

It is thus known to use ultrafiltration to separate compounds having a large molar mass, such as lignosulphonates present in a sulphite spent liquor, from compounds having a small molar mass, such as xylose, whereby

compounds having a large molar mass (lignosulphonates) are separated into the retentate and compounds having a small molar mass (xylose) are enriched into the permeate. Further enriching of xylose from e.g. salts is possible for example with chromatographic methods using ion exclusion.

5 Nanofiltration is a relatively new pressure-driven membrane filtration process, falling between reverse osmosis and ultrafiltration. Nanofiltration typically retains large and organic molecules with a molar mass greater than 300 g/mol. The most important nanofiltration membranes are composite membranes made by interfacial polymerisation. Polyether sulfone membranes, 10 sulfonated polyether sulfone membranes, polyester membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes are examples of widely used nanofiltration membranes. Inorganic and ceramic membranes can also be used for nanofiltration.

15 U.S. Patent 5,869,297 (Archer Daniels Midland Co.) discloses a nanofiltration process for making dextrose. This process comprises nanofiltering a dextrose composition including as impurities higher saccharides, such as disaccharides and trisaccharides. A dextrose composition having a solids content of at least 99% dextrose is obtained. Crosslinked aromatic polyamide 20 membranes have been used as nanofiltration membranes.

WO 99/28490 (Novo Nordisk AS) discloses a method for enzymatic reaction of saccharides and for nanofiltration of the enzymatically treated saccharide solution including monosaccharides, disaccharides, trisaccharides and higher saccharides. Monosaccharides are obtained in the permeate, while an 25 oligosaccharide syrup containing disaccharides and higher saccharides is obtained in the retentate. The retentate including the disaccharides and higher saccharides is recovered. A thin film composite polysulfone membrane having a cut-off size less than 100 g/mol has been used as the nanofiltration membrane, for example.

30 U.S. Patent 4,511,654 (UOP Inc.) relates to a process for the production of a high glucose or maltose syrup by treating a glucose/maltose-containing feedstock with an enzyme selected from amyloglucosidase and β -amylase to form a partially hydrolyzed reaction mixture, passing the resultant partially hydrolyzed reaction mixture through an ultrafiltration membrane to 35 form a retentate and a permeate, recycling the retentate to the enzyme treat-

ment stage, and recovering the permeate including the high glucose or maltose syrup.

U.S. Patent 6,126,754 (Roquette Freres) relates to a process for the manufacture of a starch hydrolysate with a high dextrose content. In this process, a starch milk is subjected to enzymatic treatment to obtain a raw saccharified hydrolysate. The hydrolysate thus obtained is then subjected to nanofiltering to collect as the nanofiltration permeate the desired starch hydrolysate with a high dextrose content.

Brief Summary of the Invention

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The purpose of the invention is to provide a method of separating chemical compounds having a small molar mass from compounds having only a slightly larger molar mass. The purpose of the present invention is also to provide a method of recovering xylose from a biomass hydrolysate, such as a spent liquor obtained from a pulping process. The process of the claimed invention is preferably based on the use of nanofiltration.

In accordance with the present invention, complicated and cumbersome chromatographic or ion-exchange steps can be completely or partly replaced by less complicated nanofiltration membrane techniques. The process of the invention provides a solution enriched in compounds with a small molar mass and essentially free from compounds with a slightly larger molar mass. The process of the present invention also provides a xylose solution enriched in xylose and free from conventional impurities of biomass hydrolysates, such as those present in a spent sulphite pulping liquor.

A more detailed explanation of the invention is provided in the following description and appended claims.

Detailed Description of the Invention

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A detailed description of preferred embodiments of the invention will now be explained.

The invention relates to a process of separating compounds having a small molar mass from compounds having a large molar mass and from compounds having a relatively large molar mass, whereby the separation is carried out using nanofiltration while simultaneously separating compounds having only a slightly larger molar mass from the compounds having a small

molar mass. In the nanofiltration in accordance with the invention, the compounds with a small molar mass are separated into the permeate, while compounds with a large molar mass, compounds with a relatively large molar mass and compounds with a slightly larger molar mass are left in the retentate.

Compounds to be separated are typically organic molecules, such as carbohydrates, especially sugars and sugar alcohols. Compounds to be separated are essentially non-charged molecules. However, in the nanofiltration process of the invention, ionic substances, especially divalent ions are simultaneously separated from the compounds with a small molar mass into the retentate.

Compounds with a small molar mass typically refer to pentoses, such as xylose and arabinose. Compounds with a slightly larger molar mass refer to compounds having a molar mass of up to 2 times, preferably up to 1.5 times that of the compounds with a small molar mass. Compounds with a slightly larger molar mass are typically hexoses, such as glucose, galactose, rhamnose and mannose.

Compounds with a large molar mass refer to compounds having a molar mass over 4 times that of the compounds with a small molar mass, such as lignosulphonates. Compounds with a relatively large molar mass refer to compounds having a molar mass of 2 to 4 times that of the compounds with a small molar mass, such as oligosaccharides.

In the nanofiltration of the invention, ionic substances, such as divalent ions are typically left in the retentate. In the process of the invention, ionic substances are thus simultaneously separated from the compounds with a small molar mass.

The compounds to be separated in accordance with the process of the invention are typically present in a biomass hydrolysate, such as a spent liquor obtained from a pulping process.

In a preferred embodiment of the invention, the invention relates to a process of producing a xylose solution from a biomass hydrolysate. The process of the invention is characterized by nanofiltering said biomass hydrolysate and recovering as the permeate a solution enriched in xylose.

The biomass hydrolysate useful in the present invention is obtained from the hydrolysis of any biomass, typically xylan-containing vegetable material. The biomass hydrolysate can be obtained from the direct acid hydrolysis

of biomass, from enzymatic or acid hydrolysis of a prehydrolysate obtained from biomass by prehydrolysis (with steam or acetic acid, for instance), and from sulphite pulping processes. Xylan-containing vegetable material include wood material from various wood species, particularly hardwood, such as birch, aspen and beech, various parts of grain (such as straw and husks, particularly corn and barley husks and corn cobs and corn fibers), bagasse, coconut shells, cottonseed skins etc.

In the process of the present invention, a xylose solution having a xylose content of over 1.1 times, preferably over 1.5 times, most preferably over 2.5 times that of the starting biomass hydrolysate (based on the dry substance content) is obtained, depending e.g. on the xylose content and pH of the biomass hydrolysate and the nanofiltration membrane used. Typically, a xylose solution having a xylose content of or over 1.5 to 2.5 times that of the starting biomass hydrolysate (based on the dry substance content) is obtained, depending e.g. on the xylose content and pH of the biomass hydrolysate and the nanofiltration membrane used.

The biomass hydrolysate used for the recovery of xylose in accordance with the present invention is typically a spent liquor obtained from a pulping process. The spent liquor is especially a spent sulphite pulping liquor, especially an acid spent sulphite pulping liquor. The spent sulphite pulping liquor is typically obtained from hardwood sulphite pulping.

The dry substance content of the starting biomass hydrolysate, such as spent liquor is typically 5 to 50 % by weight, preferably 8 to 25% by weight.

The xylose content of the spent liquor to be treated is typically 10 to 40% by weight, based on the dry substance content. A spent liquor obtained directly from hardwood sulphite pulping has a typical xylose content of 10 to 20 %, based on the dry substance content.

The spent hardwood sulphite pulping liquor also contains other monosaccharides in a typical amount of 10 to 30%, based on the xylose content. Said other monosaccharides include e.g. glucose, galactose, rhamnose, arabinose and mannose. Furthermore, the spent hardwood sulphite pulping liquor typically includes rests of pulping chemicals and reaction products of the pulping chemicals, lignosulphonates, oligosaccharides, disaccharides, xylonic acid, uronic acids, metal cations, such as calcium and magnesium cations,

and sulphate and sulphite ions. The biomass hydrolysate used as starting material also contains rests of acids used for the hydrolysis of the biomass.

The spent liquor to be treated is typically a xylose-containing spent liquor obtained from a pulping process. A typical spent liquor useful in the present invention is a xylose-containing spent sulphite pulping liquor, which is preferably obtained from acid sulphite pulping. The spent liquor may be obtained directly from sulphite pulping. It may also be a concentrated sulphite pulping liquor or a side-relief obtained from sulphite cooking. It may also be a xylose-containing fraction chromatographically obtained from a sulphite pulping liquor or a permeate obtained by ultrafiltration of a sulphite pulping liquor. Furthermore, a post-hydrolyzed spent liquor obtained from neutral cooking is suitable.

The spent liquor useful in the present invention is preferably obtained from hardwood pulping. A spent liquor obtained from softwood pulping is also suitable, preferably after hexoses have been removed e.g. by fermentation.

In the present invention, the spent liquor to be treated may also be any other liquor obtained from the digestion or hydrolysis of biomass, typically cellulosic material with an acid. Such a hydrolysate can be obtained from cellulosic material for example by treatment with an inorganic acid, such as hydrochloric acid, sulphuric acid or sulphur dioxide, or by treatment with an organic acid, such as formic acid or acetic acid. A spent liquor obtained from a solvent-based pulping, such as ethanol-based pulping may also be used.

The process may also comprise one or more pretreatment steps. The pretreatment before the nanofiltration is typically selected from ultrafiltration, chromatography, concentration, pH adjustment, filtration, dilution and combinations thereof. Before the nanofiltration, the starting liquor is thus preferably pretreated by ultrafiltration or chromatography, for example. Furthermore, a prefiltering step to remove the solid substances can be used before the nanofiltration. The pretreatment of the starting liquor may also comprise concentration, e.g. by evaporation, and neutralization. The pretreatment may also comprise crystallization, whereby the starting liquor may also be a mother liquor obtained from the crystallization of xylose, for example.

The nanofiltration is typically carried out at a pH of 1 to 7, preferably 3 to 6.5, most preferably 5 to 6.5. The pH depends on the composition of the starting biomass hydrolysate and the membrane used for the nanofiltration

and the stability of sugars or components to be recovered. If necessary, the pH of the spent liquor is adjusted to the desired value before nanofiltration using preferably the same reagent as in the pulping stage, such as $\text{Ca}(\text{OH})_2$ or MgO , for example.

5 The nanofiltration is typically carried out at a pressure of 10 to 50 bar, preferably 15 to 35 bar. A typical nanofiltration temperature is 5 to 95°C , preferably 30 to 60°C . The nanofiltration is typically carried out with a flux of 10 to $100 \text{ l/m}^2\text{h}$.

10 The nanofiltration membrane used in the present invention can be selected from polymeric and inorganic membranes having a cut-off size of 100 - 2500 g/mol , preferably 150 to 1000 g/mol , most preferably 150 to 500 g/mol .

15 Typical polymeric nanofiltration membranes useful in the present invention include, for example, polyether sulfone membranes, sulfonated polyether sulfone membranes, polyester membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes and combinations thereof.

 Typical inorganic membranes include ZrO_2 - and Al_2O_3 -membranes, for example.

20 Preferred nanofiltration membranes are selected from sulfonated polysulfone membranes and polypiperazine membranes. For example, specific useful membranes are: Desal-5 DK nanofiltration membrane (manufacturer Osmonics) and NF-200 nanofiltration membrane (manufacturer Dow Deutschland), for example.

25 The nanofiltration membranes which are useful in the present invention may have a negative or positive charge. The membranes may be ionic membranes, i.e. they may contain cationic or anionic groups, but even neutral membranes are useful.

30 The typical form of nanofiltration membranes is a flat sheet form. The membrane configuration may also be selected e.g. from tubes, spiral membranes and hollow fibers. "High shear" membranes, such as vibrating membranes and rotating membranes can also be used.

 Before the nanofiltration procedure, the nanofiltration membranes may be pretreated with alkaline detergents or ethanol, for example.

35 In a typical nanofiltration operation, the liquor to be treated, such as a spent liquor is fed through the nanofiltration membrane using the temperature and pressure conditions described above. The liquor is thus fractionated

into a low molar mass fraction including xylose (permeate) and a high molar mass fraction including the non-desired components of the spent liquor (retentate).

The nanofiltration equipment useful in the present invention comprises at least one nanofiltration membrane element dividing the feed into a retentate and permeate section. The nanofiltration equipment typically also include means for controlling the pressure and flow, such as pumps and valves and flow and pressure meters. The equipment may also include several nanofiltration membrane elements in different combinations, arranged in parallel or series.

The flux of the permeate varies in accordance with the pressure. In general, at a normal operation range, the higher the pressure, the higher the flux. The flux also varies with the temperature. An increase of the operating temperature increases the flux. However, with higher temperatures and with higher pressures there is an increased tendency for a membrane rupture. For inorganic membranes, higher temperatures and pressures and higher pH ranges can be used than for polymeric membranes.

The nanofiltration in accordance with the present invention can be carried out batchwise or continuously. The nanofiltration procedure can be repeated once or several times. Recycling of the permeate and/or the retentate back to the feed vessel (total recycling mode filtration) can also be used.

After nanofiltration, the xylose may be recovered from the permeate, e.g. by crystallization. The nanofiltered solution can be used as such for the crystallization, without further purification and separation steps. If desired, the nanofiltered xylose-containing liquor can be subjected to further purification, e.g. by chromatography, ion exchange, concentration by evaporation or reverse osmosis, or colour removal. The xylose may also be subjected to reduction, e.g. by catalytic hydrogenation, to obtain xylitol.

The process may also comprise a further step of recovering a solution rich in lignosulphonates, hexoses, oligosaccharides and salts as the retentate.

In a typical embodiment the invention, a solution enriched in pentoses is recovered as the permeate and a solution enriched in hexoses is recovered as the retentate. Furthermore, a solution enriched in divalent salts is obtained as the retentate.

The present invention also provides a method of regulating the xylose content of the permeate by regulating the dry substance content of the biomass hydrolysate, such as a spent liquor.

The invention also relates to the xylose solution obtained by the present invention. Furthermore, the invention relates to the use of the xylose solution thus obtained for the preparation of xylitol. Xylitol is obtained by reducing the xylose product obtained, e.g. by catalytic hydrogenation.

Preferred embodiments of the invention will be described in greater detail by the following examples, which are not construed as limiting the scope of the invention.

In the examples and throughout the specification and claims, the following definitions have been used:

DS refers to the dry substance content measured by Karl Fischer titration, expressed as % by weight.

RDS refers to the refractometric dry substance content, expressed as % by weight.

Flux refers to the amount (liters) of the solution that permeates through the nanofiltration membrane during one hour calculated per one square meter of the membrane surface, l / (m²h).

Fouling refers to the percentage difference in the flux values of pure water measured before and after the nanofiltration:

$$\text{fouling (\%)} = [(PWFb - PWFa) / PWFb] \times 100,$$

where PWFb is the flux of pure water before the nanofiltration of the xylose solution and PWFa is the flux of pure water after the nanofiltration of xylose solution under the same pressure.

Retention refers to the proportion of the measured compound retained by the membrane. The higher the retention value, the less is the amount of the compound transferred through the membrane:

$$\text{Retention (\%)} = [(\text{Feed} - \text{Permeate}) / \text{Feed}] \times 100,$$

where "Feed" refers to the concentration of the compound in the feed solution (expressed e.g. in g/l) and "Permeate" refers to the concentration of the compound in the permeate solution (expressed e.g. in g/l).

HPLC refers to liquid chromatography.

The following membranes were used in the examples:

- Desal-5 DK (a four-layered membrane consisting of a polyester layer, a polysulfone layer and two proprietary layers, having a cut-off size of

150 to 300 g/mol, permeability (25 °C) of 5.4 l/(m²h bar) and MgSO₄-retention of 98 % (2 g/l), manufacturer Osmonics),

- Desal-5 DL (a four-layered membrane consisting of a polyester layer, a polysulfone layer and two proprietary layers, having a cut-off size of 150 to 300 g/mol, permeability (25°C) of 7.6 l/(m²h bar), MgSO₄-retention of 96% (2 g/l), manufacturer Osmonics),

- NTR-7450 (a sulfonated polyethersulfone membrane having a cut-off size of 500 to 1000 g/mol, permeability (25°C) of 9.4 l/(m²h bar), NaCl-retention of 51% (5 g/l), manufacturer Nitto Denko), and

- NF-200 (a polypiperazine membrane having a cut-off size of 200 g/mol, permeability (25°C) of 7 - 8 l/(m²h bar), NaCl-retention of 70%, manufacturer Dow Deutschland).

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EXAMPLE I.

Nanofiltration of a spent sulphite pulping liquor using various membranes at various pH values

This example illustrates the effect of the membrane and pH on the performance of nanofiltration (filtrations C1, C3, C6 and C8). The liquor to be treated was a diluted runoff of the crystallization of a Mg-based sulphite spent pulping liquor obtained from beechwood pulping, which had been chromatographically purified using an ion exchange resin in Mg²⁺ form. The pH of the solution was adjusted to the desired value (see Table I) with MgO. Before the nanofiltration, the liquor was pretreated by dilution (filtrations C1 and C3), by filtration through a filter paper (filtration C6) or with MgO dosing combined with filtration through a filter paper (filtrations C7 and C8).

A batch mode nanofiltration was carried out using a laboratory nanofiltration equipment consisting of rectangular cross-flow flat sheet modules with a membrane area of 0.0046 m². Both the permeate and the retentate were recycled back to the feed vessel (total recycling mode filtration). The feed volume was 20 liters. During the filtration, the cross-flow velocity was 6 m/s and the pressure was 18 bar. The temperature was kept at 40 °C.

Table I presents the results of the total recycling mode filtrations. The flux values in Table I were measured after 3 hours of filtration. Table I shows the dry substance content (DS) in the feed (%), the xylose content in

the feed and in the permeate (based on the dry substance content), the permeate flux at a pressure of 18 bar and the flux reduction caused by fouling. The membranes were Desal-5 DK and NTR-7450.

TABLE I

Filtration No., membrane	pH	DS in the feed, w-%	Xylose in feed, % on DS	Xylose in permeate, % on RDS	Flux l/(m ² h)	Fouling, %
C1, Desal-5 - DK	3.4	8.1	22.6	27.4	31	1
C6* Desal-5-DK	3.4	9.7	20.3	33.5	23	1
C7* Desal-5-DK	5.9	8.2	21.7	55.2	58	3
C3, NTR-7450	3.4	7.6	24.3	29.9	25	29
C8, NTR-7450	6.1	8.3	21.8	34.5	43	25
C8, Desal-5-DK	6.1	8.3	21.8	45	30	1

* average value of two membranes

- 5 The results of Table I show that nanofiltration provides xylose concentrations of 1.5 to 2.5 times those of the feed. When the pH in the feed is high, the xylose content on RDS in the permeate is high. The xylose content on RDS in the permeate is high for example when pH is 5.9 or 6.1. Furthermore, the flux was improved even to two-fold at higher pH values. The Desal-5
- 10 DK membrane at a high pH provided the best results.

EXAMPLE II

Nanofiltration at various temperatures

The effect of the temperature was studied using the same equipment and the same spent liquor solution as in Example 1. The temperature during the nanofiltration was raised from 25°C to 55°C. The membrane was Desal-5 DK, and the nanofiltration conditions were the following: pH 3.4, pressure 16 bar, cross-flow velocity 6 m/s, DS 7.8%. The feed concentration and pressure were kept constant during the experiment.

Table II shows the xylose contents in the feed and in the permeate, based on the dry substance content (permeate values are average values of two membranes).

TABLE II

Temperature, °C	Xylose in feed, % on DS	Xylose in permeate, % on RDS
25	24.5	23.8
40	24.5	29.9
55	24.6	34.6

The results of Table II show that the higher the temperature, the higher concentrations of xylose can be obtained.

EXAMPLE III

(A) Pretreatment with ultrafiltration

Concentration mode ultrafiltrations DU1 and DU2 were carried out using an RE filter (rotation-enhanced filter). In this filter, the blade rotates near the membrane surface minimizing the concentration polarization during the filtration. The filter was a home-made cross-rotational filter. The rotor speed was 700 rpm. In filtration DU1, the membrane was C5F UF (a membrane of regenerated cellulose having a cut-off size of 5000 g/mol, manufacturer Hoechst/Celgard). In filtration DU2, the membrane was Desal G10 (a thin film membrane having a cut-off size of 2500 g/mol, manufacturer Osmonics/Desal).

Concentration mode filtrations were made using a Mg-based sulphite spent pulping liquor obtained from beechwood pulping. The filtration was

carried out at a temperature of 35°C and a pH of 3.6. The results are presented in Table IIIa.

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Table IIIa

Filtration No.	Membrane	DS in feed, %	Filtration time	Xylose in feed, % on DS	Xylose in permeate, % on RDS
DU1	C5F	14.4	1 hour	16.3	23.2
DU1	C5F	22.0	23 hours	9.2	20.0
DU2	Desal G10	12.2	3 days	12.7	41.6

(B) Nanofiltration

5 A one-day laboratory-scale experiment where the permeate was collected out was carried out with the same equipment as in Example 1 (filtrations DN1 and DN2). The liquor to be treated was a Mg-based sulphite spent pulping liquor obtained from beechwood pulping.

10 In filtration DN1, the ultrafiltered spent liquor (DU1 using a C5F membrane) was used as the feed solution. The pH of the solution was adjusted to 4.5 using MgO, and the liquor was prefiltered through a filter paper before nanofiltration. Nanofiltration was carried out at a pressure of 19 bar and at a temperature of 40°C.

15 Filtration DN2 was carried out using the diluted original spent liquor. Its pH had been adjusted to 4.8 and the solution was prefiltered through a filter paper before nanofiltration. The nanofiltration was carried out at a pressure of 17 bar and at a temperature of 40°C. After about 20 hours of filtration, a permeate volume of 5 liters and a concentrate volume of 20 liters were obtained.

20 Both filtrations DN1 and DN2 were carried out at a cross-flow velocity of 6 m/s. Fouling was about 1% in both filtrations. The nanofiltration membrane in both filtrations was Desal-5 DK.

25 In each filtration DN1 and DN2, the nanofiltration membrane was pretreated in three different ways: (1) no pretreatment, (2) washing the membrane with ethanol, and (3) washing the membrane with an alkaline detergent.

The results are set forth in Table IIIb:

TABLE IIIb

Filtration	pH	DS in feed, %	Xylose in feed, % on DS	Xylose in permeate, % on RDS (1)/(2)/(3)	Flux, l/(m ² h) at 20 h
DN1	4.5	10.7	21.1	24/35/49	14 (19 bar)
DN2	4.6	12.3	16.8	N.A.*/35/34	22/32 (17/19 bar)

* (N.A. = not analyzed)

- 5 The results of Table IIIb show that the proportion of xylose in the dry solids of the permeate obtained from the nanofiltration was somewhat changed when ultrafiltration was used as a pretreatment step. On the other hand, washing the membrane with ethanol or an alkaline detergent increased the xylose content considerably.

10

EXAMPLE IV

Nanofiltration at various pressures

- Experiment DS1 was carried out using DSS Labstak® M20-filtering equipment operating with total recycling mode filtration (manufacturer Danish Separation Systems AS, Denmark). The liquor to be treated was the same as in Example III. The temperature was 35°C and the flow rate was 4.6 l/min. The membrane was Desal-5 DK. Before the experiments, the pH of the spent liquor was adjusted to 4.5 and the liquor was prefiltered through a filter paper.

The results are shown in Table IVa.

20

Table IVa

Filtration	Pressure	DS in feed, % on DS	Xylose in feed, % on DS	Xylose in per- meate, % on RDS	Flux, l/(m ² h)
DS1	22 bar	11.4	17.3	24.5	18
	35 bar	12.1	16.5	20.9	42

Further experiments (filtrations DV1 and DV2) were carried out using a VØSEP filter (manufacturer New Logic), which is a high shear rate filter. Its efficiency is based on vibrating motion that causes a high shear force on the membrane surface. In filtration DV1, the feed concentration has been increased during the filtration by adding new concentrated feed to the vessel. At the same time the pressure was also increased. Table V shows the xylose content based on the dry solids contents in the feed and in the permeate at two feed dry solids concentrations.

TABLE IVb

Filtration	DS in feed, %	Pressure, bar	Xylose in feed, % on DS	Xylose in permeate, % on RDS	Flux, l/(m ² h)
DV1	11	21	16	20	75
DV2	21	35	16	42	22

It can be seen from the results of Tables IVa and IVb that a simultaneous increase of the nanofiltration pressure and the dry substance content of the feed increased the xylose content of the permeate.

EXAMPLE V

Nanofiltration at various values of the feed dry solids

The liquor to be treated was the ultrafiltered liquor from filtration DU2 of Example III (the ultrafiltration had been carried out with Desal G10 membrane from Osmonics/Desal). The nanofiltration was carried out at a pressure of 30 bar, a temperature of 35°C and a pH of 5.3). The nanofiltration membranes were Desal-5 DK, Desal-5 DL and NF 200.

The effect of feed dry solids content on the membrane performance is presented in Table V.

TABLE V

5

DS in feed, %	Xylose in feed, % on DS	Xylose in permeate, % on DS		
		Desal-5DK	Desal-5 DL	NF 200
5.6	33.2	31	26	42
10.3	32.5	42	35	60
18.5	29.8	69	65	64

For comparative purposes, the contents of other carbohydrates (in addition to xylose), oligosaccharides, xylonic acid, metal cations (Ca^{2+} and Mg^{2+}) as well as sulphite and sulphate ions were analyzed from samples taken from a concentration mode ultrafiltration (DS4) at three different concentrations (the feed samples) and from the corresponding permeates obtained from nanofiltration with three different nanofiltration membranes (the permeate samples).

The results are set forth in Table Va. In Table Va, sample numbers A, B and C refer to samples taken from the feed (liquor ultrafiltered with Desal G10 membrane) in a concentration mode filtration at three different dry substance contents (DS) of 5.6, 10.3 and 18.5, sample numbers D, E and F refer to corresponding samples taken from the permeate obtained from nanofiltration with a Desal 5DK membrane, sample numbers G, H and I refer to corresponding samples taken from the permeate obtained from nanofiltration with a Desal-5 DL membrane, and sample numbers J, K and L refer to the corresponding samples taken from the permeate obtained from nanofiltration with a NF 200 membrane.

In Table Va, the contents of carbohydrates were analyzed using HPLC with Pb^{2+} form ion exchange column and RI detection, disaccharides using HPLC with Na^+ form ion exchange column and the contents of xylonic acid using HPLC with anion exchange column and PED detection.

Furthermore, Table Vb shows the carbohydrate contents and some other analytical results of the feed liquid at a dry substance content of 18.5% (sample C above) and of the corresponding permeate samples (samples F, I

and L above) (ultrafiltration as the pretreatment step; the nanofiltering conditions: 35 °C, 30 bar, pH 5,3, DS in the feed 18.5%, DSS LabStak® M20).

Table Va

	A	B	C	D	E	F	G	H	I	J	K	L
	DS4. S1	DS4. S2	DS4. S3	DS4. DK1	DS4. DK2	DS4. DK3	DS4. DL1	DS4. DL2	DS4. DL3	DS4. NF1	DS4. NF2	DS4. NF3
Carbohydrates, % on DS												
- glucose	3.0	3.8	3.9	1	1.4	2.8	1	1	1.9	2	3	3.9
- xylose	33.2	32.5	29.8	31	42	69	26	35	65	42	60	64.0
- galactose + rhamnose	1.9	1.9	1.9	0.7	1.0	1.6	0.7	0.9	1.5	1	1.5	2.1
- arabinose	0.3	0.3	0.3	0.3	0.3	0.6	n.a.	0.3	0.7	0.5	0.6	0.5
- mannose	3.2	3.2	3.3	1	1.5	2.7	1	1.5	2.6	2	3	3.2
Disaccharides, % on DS	0.5	0.5	0.5	n.d.	0.2	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
Xylonic acid, % on DS	11.5	11.6	12.7	5	5	4	5	5	5	5	5	4.1
Metals (ICP), % on DS												
- Ca	0.12	0.11	0.11	0.7	0.4	0.1	0.7	0.5	0.1	0.4	0.3	0.1
- Mg	2.1	4.0	4.6	0.5	0.4	0.04	0.9	0.9	0.3	2.1	2.6	2.5
Sulphite (IC), % on DS	0.51	0.62	0.59	0.4	0.3	0.5	0.5	0.4	0.6	0.3	0.6	0.9
Sulphate (IC), % on DS	2.9	3.2	3.8	0.2	0.2	0.1	1	0.8	0.5	0.6	0.5	0.4

n.a. = not analyzed

n.d. = not detected

TABLE Vb

	Feed	Permeate		
	UF permeate (sample C)	Desal-5 DK (sample F)	Desal-5 DL (sample I)	NF-200 (sample L)
pH	5.4	4.8	4.9	5.2
Conductivity, mS/cm	13.1	2.2	2.8	4.5
Colour I	99300	7050	12200	7540
UV 280 nm, 1/cm	350	17	16	18
Xylose, % on DS	29.8	69.0	65.0	64.0
Glucose, % on DS	3.9	2.8	1.9	3.9
Xylonic acid, % on DS	12.7	4.0	5	4.1
Mg ²⁺ , % on DS	4.6	0.04	0.3	2.5
SO ₄ ²⁻ , % on DS	3.8	0.1	0.5	0.4

Tables Va and Vb show that nanofiltration effectively concentrated pentoses, such as xylose and arabinose in the permeate, while removing an essential amount of disaccharides, xylonic acid, magnesium and sulphate ions from the xylose solution. Hexoses, such as glucose, galactose, rhamnose and mannose were not concentrated in the permeate.

The purity of xylose solutions can thus be effectively increased by nanofiltration. Furthermore, nanofiltration demineralizes the spent liquor by removing 98% of the divalent ions.

The foregoing general discussion and experimental examples are only intended to be illustrative of the present invention, and not to be considered as limiting. Other variations within the spirit and scope of this invention are possible and will present themselves to those skilled in the art.

Claims:

1. A process of separating compounds having a small molar mass from compounds having a large molar mass and from compounds having a relatively large molar mass, c h a r a c t e r i z e d in that the separation is carried out using nanofiltration while simultaneously separating compounds having only a slightly larger molar mass from the compounds having a small molar mass.

2. A process as claimed in claim 1, c h a r a c t e r i z e d in that the compounds with a small molar mass are separated into the permeate and compounds with a large molar mass, compounds with a relatively large molar mass and compounds with a slightly larger molar mass are left in the retentate.

3. A process as claimed in claim 1 or 2, c h a r a c t e r i z e d in that the compounds to be separated are organic molecules.

4. A process as claimed in claim 3, c h a r a c t e r i z e d in that the organic molecules are carbohydrates.

5. A process as claimed in claim 4, c h a r a c t e r i z e d in that the carbohydrates are selected from sugars and sugar alcohols.

6. A process as claimed in any one of claims 1 to 5, c h a r a c t e r i z e d in that compounds to be separated are essentially non-charged molecules.

7. A process as claimed in any one of claims 1 to 6, c h a r a c t e r i z e d in that compounds with a slightly larger molar mass are compounds having a molar mass of up to 2 times, preferably up to 1.5 times that of the compounds with a small molar mass.

8. A process as claimed in any one of claims 1 to 7, c h a r a c t e r i z e d in that compounds with a small molar mass comprise pentoses and compounds with a slightly larger molar mass comprise hexoses.

9. A process as claimed in claim 8, c h a r a c t e r i z e d in that pentoses comprise xylose and arabinose and hexoses comprise glucose, galactose, rhamnose and mannose.

10. A process as claimed in any one of claims 1 to 9, c h a r a c t e r i z e d in that ionic substances are separated simultaneously from compounds with a small molar mass.

11. A process as claimed in claim 10, characterized in that ionic substances are left in the retentate.

12. A process as claimed in claim 10 or 11, characterized in that ionic substances are divalent ions.

5 13. A process as claimed in any one of claims 1 to 12, characterized in that the compounds to be separated are present in a biomass hydrolysate.

14. A process as claimed in claim 13, characterized in that the compounds to be separated are present in a spent liquor obtained from a
10 pulping process.

15. A process for producing a xylose solution from a biomass hydrolysate, characterized by nanofiltering said biomass hydrolysate and recovering as the permeate a solution enriched in xylose.

16. A process as claimed in claim 15, characterized by recovering a xylose solution having a xylose content of over 1.1 times, preferably over 1.5 times, most preferably over 2.5 times that of the starting biomass hydrolysate, based on the dry substance content.

17. A process as claimed in claim 16, characterized by recovering a xylose solution having a xylose content of or over 1.5 to 2.5 times that of the starting biomass hydrolysate, based on the dry substance content.
20

18. A process as claimed in any one of claims 15 to 17, characterized in that the dry substance content of the starting biomass hydrolysate is 3 to 50 % by weight, preferably 8 to 25 % by weight.

19. A process as claimed in claim 15, characterized in that
25 the biomass hydrolysate has a xylose content of 10 to 40 % by weight, based on the dry substance content.

20. A process as claimed in any one of claims 15 to 19, characterized in that the biomass hydrolysate is a spent liquor obtained from a pulping process.

30 21. A process as claimed in claim 14 or 20, characterized in that the spent liquor obtained from a pulping process is a spent sulphite pulping liquor.

22. A process as claimed in claim 21, characterized in that the spent sulphite pulping liquor is an acid spent sulphite pulping liquor.

23. A process as claimed in claim 21 or 22, characterized in that the spent sulphite pulping liquor is obtained from hardwood sulphite pulping.

24. A process as claimed in claim 20, characterized in that
5 the spent liquor is a mother liquor obtained from the crystallization of xylose.

25. A process as claimed in any one of the preceding claims, characterized in that the process also comprises one or more pretreatment steps.

26. A process as claimed in claim 25, characterized in that
10 the pretreatment is selected from ultrafiltration, chromatography, concentration, pH adjustment, filtration and combinations thereof.

27. A process as claimed in any one of the preceding claims, characterized in that nanofiltration is carried out at a pH of 1 to 7, preferably 3 to 6.5, most preferably 5 to 6.5.

28. A process as claimed in any one of the preceding claims,
15 characterized in that nanofiltration is carried out at a pressure of 10 to 50 bar, preferably 15 to 35 bar.

29. A process as claimed in any one of the preceding claims, characterized in that nanofiltration is carried out at a temperature of 5
20 - 95 °C, preferably 30 to 60 °C.

30. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration is carried out with a flux of 10 to 100 liters/m²h.

31. A process as claimed in any one of the preceding claims,
25 characterized in that nanofiltration is carried out using a nanofiltration membrane selected from polymeric and inorganic membranes having a cut-off size of 100 to 2500 g/mol.

32. A process as claimed in claim 31, characterized in that the cut-off size of the nanofiltration membrane is 150 to 1000 g/mol.

33. A process as claimed in claim 32, characterized in that
30 the cut-off size of the nanofiltration membrane is 150 to 500 g/mol.

34. A process as claimed in any one of claims 31 to 33, characterized in that the nanofiltration membranes are ionic membranes.

35. A process as claimed in any one of claims 31 to 34, characterized in that the nanofiltration membrane is selected from polyethersulphone membranes, sulfonated polyether sulphone membranes, polyester

membranes, polysulfone membranes, aromatic polyamide membranes, polyvinyl alcohol membranes and polypiperazine membranes and combinations thereof.

36. A process as claimed in claim 35, characterized in that
5 the nanofiltration membrane is selected from sulfonated polyether sulfone membranes and polypiperazine membranes.

37. A process as claimed in claim 35 to 36, characterized in that the nanofiltration membrane is selected from NF-200 and Desal-5 DK membranes.

10 38. A process as claimed in any one of claims 31 to 37, characterized in that the form of the nanofiltration membrane is selected from sheets, tubes, spiral membranes and hollow fibers.

39. A process as claimed in any one of claims 31 to 38, characterized in that the nanofiltration membrane is selected from high shear
15 type membranes.

40. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration membrane has been pre-treated by washing.

41. A process as claimed in claim 40, characterized in that
20 the washing agent is selected from ethanol and/or an alkaline detergent.

42. A process as claimed in any one of the preceding claims, characterized in that the nanofiltration process is repeated at least once.

43. A process as claimed in any one of the preceding claims,
25 characterized in that the process is carried out batchwise or continuously.

44. A process as claimed in any one of the preceding claims, characterized in that the process is carried out using a nanofiltration equipment including several nanofiltration elements arranged in parallel or series.
30

45. A process as claimed in any one of the preceding claims, characterized in that the process also comprises an post-treatment step.

46. A process as claimed in claim 45, characterized in that
35 the post-treatment step is selected from crystallization, chromatography, concentration and colour removal.

47. A process as claimed in any one of claims 15 to 46, c h a r a c -
t e r i z e d in that the process comprises a further step of recovering a solu-
tion enriched in lignosulphonates, hexoses, oligosaccharides and salts as the
retentate.

5 48. A process as claimed in any one of claims 15 to 47, c h a r a c -
t e r i z e d in that a solution enriched in pentoses is recovered as the perme-
ate and a solution enriched in hexoses is recovered as the retentate.

 49. A process as claimed in any one of claims 15 to 48, c h a -
r a c t e r i z e d in that a solution enriched in divalent salts is recovered as
10 the retentate.

 50. A process as claimed in any one of claims 15 to 49, c h a r a c -
t e r i z e d in that the dry substance content of the biomass hydrolysate is
simultaneously regulated to increase the xylose content of the permeate.

 51. A xylose solution, c h a r a c t e r i z e d in that it is obtained by
15 a process of any one of claims 15 to 50.

 52. Use of a xylose solution as claimed in claim 51 for the prepara-
tion of xylitol.

(57) Abstract

The invention relates to a process of separating compounds with a small molar mass, such as pentoses, from compounds with a slightly larger molar mass, such as hexoses, using nanofiltration. In a specific embodiment of the invention, the invention relates to a process of producing a xylose solution from a biomass hydrolysate, such as a spent liquor obtained from a pulping process, by nanofiltering said liquor and recovering a xylose solution as the permeate.